

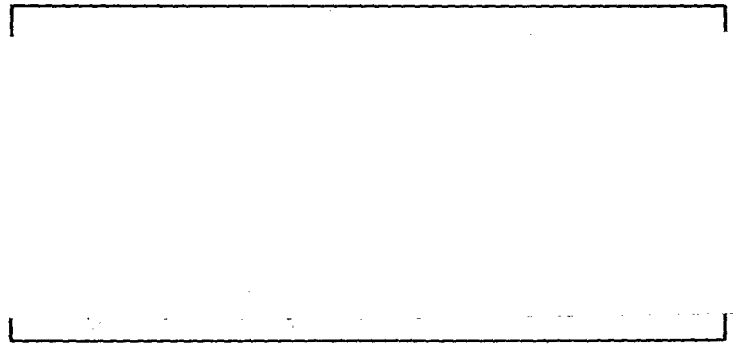
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THE INFLUENCE OF EXTRANEEOUS ELEMENTS  
IN D.C. ARC SPECTRA OF FERROUS ALLOYS

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JULY 1952

WRIGHT AIR DEVELOPMENT CENTER

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IN D.C. ARC SPECTRA OF FERROUS ALLOYS**

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*Douglas Aircraft Company, Inc.*

*July 1952*

*Materials Laboratory  
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**Wright Air Development Center  
Air Research and Development Command  
United States Air Force  
Wright-Patterson Air Force Base, Ohio**

## FOREWORD

This report was prepared by D. P. Jensen and J. F. Young of the Douglas Aircraft Company, Inc., on Contract No. AF33(038)-23304, RDO No. 606-56, "Emission Spectroanalytical Procedures". The project was administered under the direction of the Materials Laboratory, Research Division, Wright Air Development Center, with Miss N. E. Funkhouser acting as project engineer.

## ABSTRACT

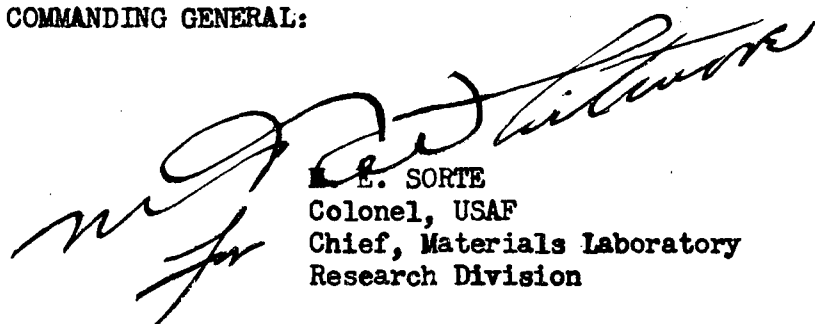
The influence of one alloying element upon the spectral line intensity of any other alloying element was subjected to investigation in the D. C. Arc. The study was carried out by making homogeneous metallic alloys in an induction furnace. Manganese, silicon, nickel, chromium, molybdenum, vanadium, aluminum and copper were used as the alloying elements in an iron matrix, with percentage magnitudes commonly found in low alloy steels. It is concluded that:

- (1) The only influence which could be attributed to any of these elements was that of copper upon the line intensity of manganese.
- (2) Oxygen contained within the metallic sample has a marked influence on the spectral line intensity of chromium.
- (3) Some other element or elements not included in this investigation such as carbon, sulfur and/or phosphorus affects the line intensities of nickel, silicon and manganese.
- (4) Alloys can be melted in an induction furnace without change in chemistry by employing the proper techniques.

## PUBLICATION REVIEW

Manuscript Copy of this report has been reviewed and found satisfactory for publication.

FOR THE COMMANDING GENERAL:



E. SORTE  
Colonel, USAF  
Chief, Materials Laboratory  
Research Division

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## INTRODUCTION

There have been many attacks on the problem of the influence of one element on the other. 1.2.3.4/ It might be said that there are almost as many answers as attacks to the problem.

Brode and Timma 3/ have suggested the possibility of establishing an ordered arrangement of elements, as in the electromotive series, with the indication that any element might have its lines depressed or enhanced by elements above or below it in the series. On the other hand numerous exceptions to such a series have been found by other writers. Duffenback, Wiley and Owens, 4/ for instance, report that sodium, potassium and magnesium were each found to depress the relative intensity of each of the others.

It is readily apparent that the results will depend a great deal on whether the sample is volatilized to completion, and in what chemical form the elements are present. In some of this previous work the method is not made clear (e.g. whether or not sample is volatilized to completion), and most of it had been made on various salts of the metals. Most of the writers acknowledge the effect of the anions on the relative line intensities, but there is also the likelihood that the chemical form may also change the influence of one element on the line intensity of another.

It was felt that for a really basic approach to this problem that elements in their elementary state should be used. We also wished to find the most reproducible D.C. arc method possible so that it could be readily standardized and applied to other work.

It was our attempt to see if a series such as that proposed by Timma and Brode could be established on elements as they occur in steels.

In order to do this it was necessary to make synthetic melts with iron as the matrix element. These melts must not only contain each element as the only alloying element, but also in combination with each of the other elements.

## SECTION I

### SPECTROGRAPHIC METHODS AND TECHNIQUES

#### I. Film Processing and Calibration

All spectrographic film used in pursuance of this program has been processed and calibrated by methods in regular use in this laboratory.

Eastman D-19 developer is stored in 250 milliliter brown bottles until ready for use. Immediately prior to using, it is poured into the developer tray and cooled to  $65 \pm 0.1^\circ\text{F}$ . The film is developed for three minutes being rocked in an A.R.L. developing machine. It is placed in Sb 1-a acetic acid short stop solution for thirty seconds then fixed for five and one half minutes in an F-5 fixing bath.

The film is washed in an A.R.L. film washer for five minutes, the outlet of which is obstructed so as to keep the washer full of water. The film is turned end to end once at the middle of this washing period. The film is rinsed with distilled water and the excess water shaken from it. It is then wiped on both sides with a damp chamois skin. The film is shaken completely dry, then placed in an A.R.L. film dryer with the heater and blower on for one and one-half minutes. After cooling for about ten minutes the film is ready to place on the densitometer and the transmissions of the proper spectral lines determined.

For all of the quantitative in the first order, Eastman Kodak Spectrum Analysis No. 2 film is used due to its negligible change in contrast with wave length. In this laboratory the contrast is calibrated by use of a rotating stepped sector, but the same method can be applied to the use of a neutral stepped filter.

In either case a steel bar is excited by means of a spark type excitation as outlined in the point-to-plane analysis of steels. It is standard practice in this laboratory to use a 60 micron slit whenever transmissions of the spectral lines are to be measured. No pre-spark is used and the film is exposed for fifteen seconds with the rotating stepped sector or a stepped filter in the light path. The film is then processed as outlined above.

After the film is placed on the densitometer, at least fifty pairs of lines in the wave length regions used in quantitative analysis are read. We shall designate the transmissions of the lines for one step of the sector or filter  $T_1$ , that of the other step as  $T_2$ . These transmissions should vary uniformly from the lowest to highest readings possible.



$T_1$  is then plotted against  $T_2$  for each of the lines measured. A preliminary curve is obtained (Figure 1, Page 7) by drawing the best line through these points. If we designate the original intensities producing the transmissions  $T_1$  and  $T_2$ ,  $I_1$  and  $I_2$  respectively, then

$$\frac{I_1}{I_2} = K \text{ where } K \text{ is a constant.}$$

Taking logarithms of both sides

$$\log I_1 - \log I_2 = \log K$$

Simply stated this means that the logarithms of the intensities for  $T_1$  and  $T_2$  have a constant difference.

This fact and the data from the curve shown in Figure 1, page 7, is used to plot the characteristic darkening curve shown in Figure 2, Page 7.

Using the A.R.L. calculating board we assume a point A (Figure 2) to the top and right of the calculating board. The transmission  $T_A$  at this point can be read off the sliding vertical log scale supplied with the calculating board. Starting with this value  $T_A$  we go to the curve shown in Figure 2 and get a series of points as follows by finding corresponding  $T_2$  for  $T_1$ .

$T_1$	$T_2$
$T_A$	$T_B$
$T_B$	$T_C$
$T_C$	$T_D$
$T_D$	----

This yields a series of transmissions  $T_A, T_B, T_C, T_D$ . The log of the original intensities corresponding to these transmissions will each vary from the preceding one by a difference of  $\log K$ . We can therefore plot points B, C, D, equally spaced along the abscissa (here we use five divisions) and at ordinate heights on the log scale of  $T_B, T_C, T_D$ .

If more points are desired for the characteristic darkening curve, a point is selected on the straight line portion of the curve and succeeding points plotted from this origin in the same manner as starting from point A.

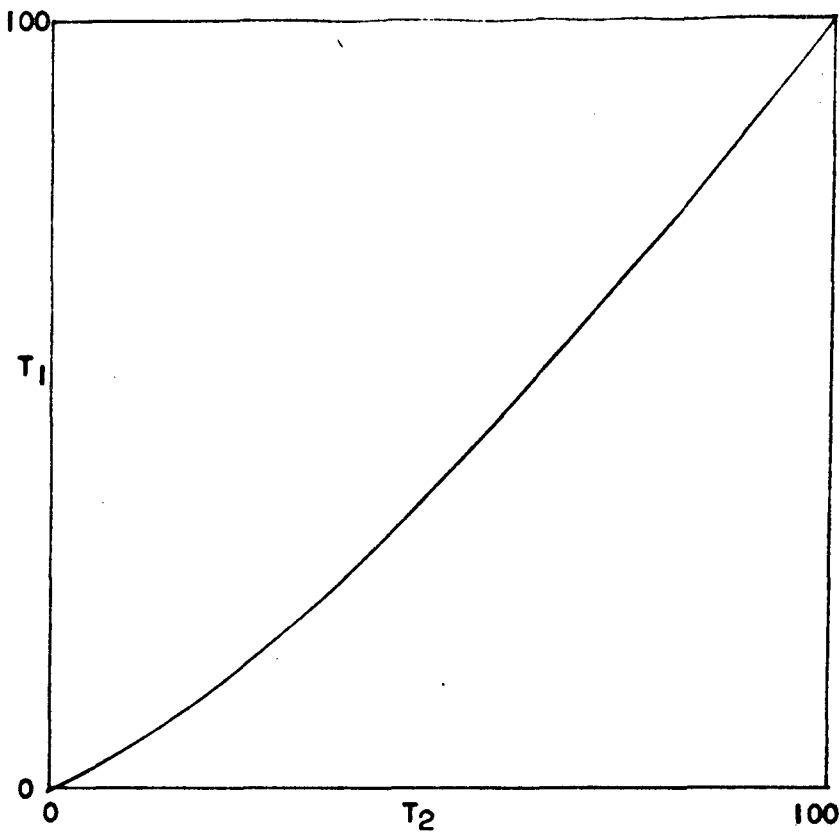


FIGURE 1 PRELIMINARY CURVE

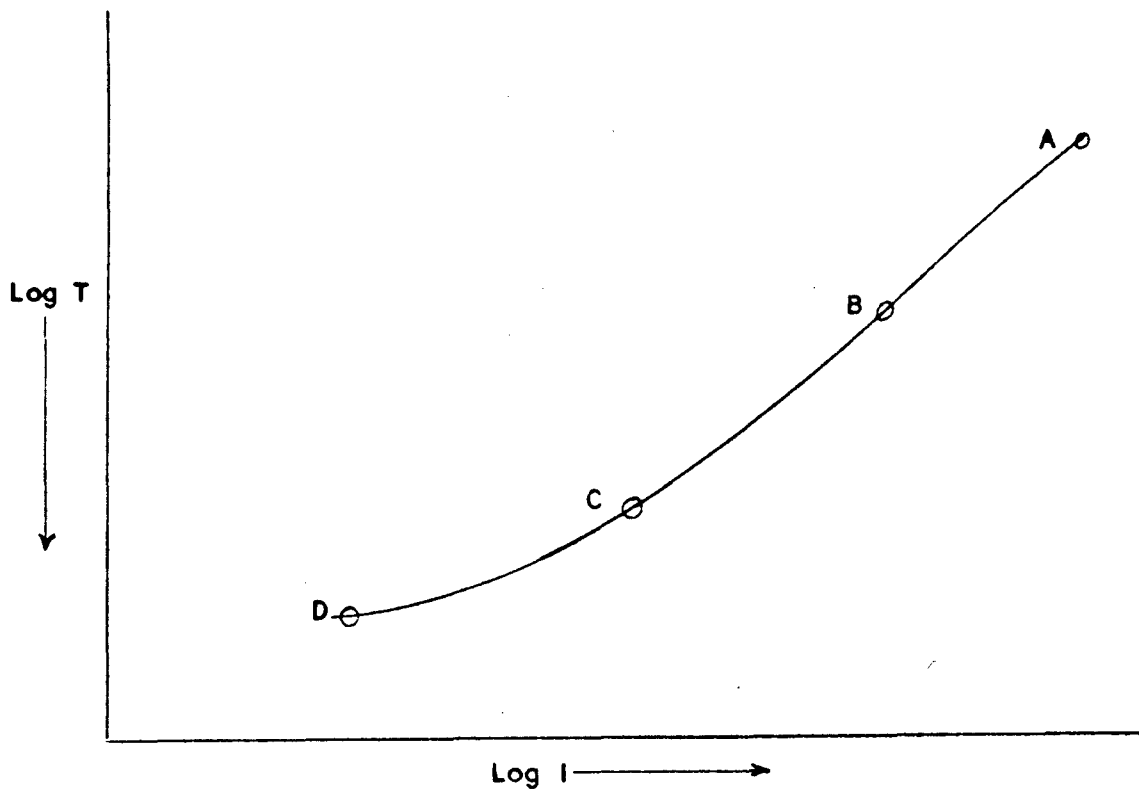


FIGURE 2 CHARACTERISTIC DARKENING CURVE

In this laboratory since the steps of the rotating sector vary from one another by fifty percent, K is equal to two. Two on the horizontal sliding log scale is equal to 7.2 divisions on the calculating board graph paper. Since 5 divisions were allowed to represent log K then the log of the intensity ratios read from this curve will vary from the log of true intensity ratios by the ratio of 5 to 7.2.

Ordinarily this correction is not made in this laboratory since the working curves will incorporate it as a constant factor in the logarithms of the intensity ratios. For the purposes of the research program, however, true intensity ratios will be given.

It has been found sufficiently accurate to determine the characteristic darkening curve only for different emulsion numbers of films.

## 2. Point-to-Plane Spark Analysis of Steel

In order to make preliminary analyses of the standards used in this program, a point-to-plane spark technique was employed. This technique has been developed over the last several years. It was found early in our work that at least a thirty seconds pre-spark is required for steel in order to obtain reliable results for manganese. Steels of the following types have been analyzed successfully: A.I.S.I. series 1000, 1100, 1300, 2300, 3100, 3300, 4000, 4100, 4300, 5200, 6100, 8600 and 8700.

In this method samples are prepared with either a Vixen Wiccut file or on an eighty grit alundum belt. In either case a flat surface is prepared at least one quarter inch in diameter. In placing the sample on the stage this flat surface must be in the same plane as the top of the stage. The counter electrode is made from .242 inch special purity graphite. It is hemispherically tipped by means of an A.R.L. #2380A Cutter. The electrode spacing is set with the sample one millimeter above the optical axis and the counter electrode one mm below giving a total electrode spacing of two mm.

The sample is made positive and the counter electrode negative and excitation supplied by the A.R.L. Multisource as follows: Voltage regulator on, Initiator continuous and high power, phasing 0-180°, pistol switch setting 1 and output voltage controlled at 940 volts. The power circuit is set at 2 microfarads capacitance, 50 microhenries inductance and 0.4 ohms (residual) resistance. The timers are set so as to pre-spark the sample for 30 seconds then expose the film for 20 seconds.

The film is processed as described previously, and the following line pairs read:

<u>Element</u>	<u>Wave Length</u>	<u>Fe Int. Std Line</u>
Mn	3460.3	3277.3
V	3110.7	3277.3
Mo	2816.2	3277.3
Cr	3118.7	3277.3
	3408.8 (when V is present)	
Ni	3414.8	3199.5
Al	3082.1	3199.5
Cu	3274.0	3199.5
Si	2881.6	3199.5

Using the characteristic darkening curve described previously, the intensity ratios of the various lines with respect to the appropriate iron lines are calculated. From these, percentage compositions are determined by means of curves previously plotted using standards run in the same manner. These curves have element percentage plotted against the intensity ratio of that element's line with respect to the appropriate iron line.

### 3. D. C. Platform-Arc

The platform-arc used in this research program is essentially that described by Hasler, Harvey and Dietert.<sup>5/</sup>

The special type of carbon electrode used as shown in Figure 3 (Page 10) allows the sample to be burned to completion, which is the only possible way to insure accuracy in a stationary arc type of discharge.

To insure good sampling and to make uniform measurements of the load, very fine filings should be made of the sample. In this laboratory a ten inch mill bastard type file is used to obtain filings from the sample. A special scoop has been drilled out to accommodate approximately three milligrams of these steel filings. Tests have shown that the weights of samples

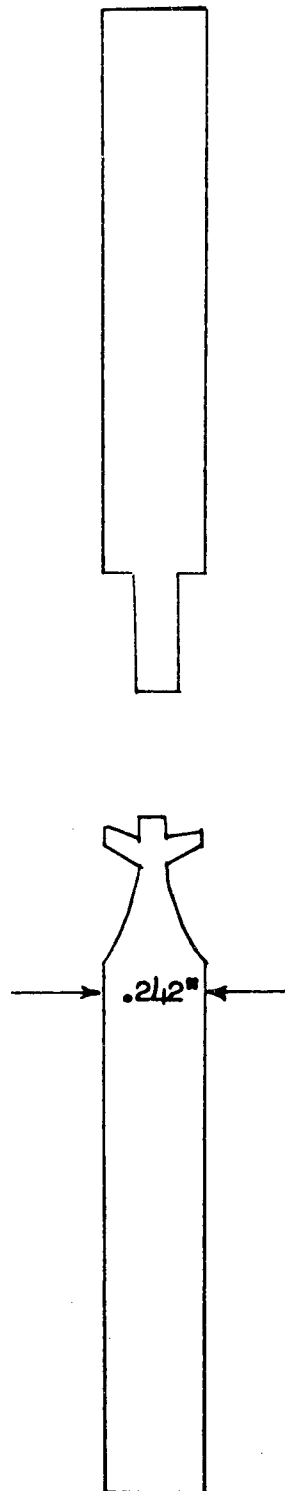


FIGURE 3

SPECIAL CARBON PLATFORM ELECTRODE

taken by this method show very little variation.

Prior to loading the platform electrode, it is pre-arc'd for ten seconds being made the cathode for this pre-arc'ing period. The three milligram sample of filings is then placed on the platform and the base of the electrode tapped lightly to distribute the sample around the center post. A drop of an alcohol sugar solution is then added. This solution consists of 30 grams sugar, 100 ml water and 100 ml alcohol. The sample may then be dried with a small flame.

The electrodes are centered accurately on the optical axis. Vertically they are one millimeter above and below the optical axis, giving a total electrode spacing of two millimeters.

Excitation is supplied by an A.R.L. Dietert Multisource. A rectifier discharge is used, the Multisource settings being as follows: Voltage regulator off, Ignitor on strike and low power, pistol switch on 2 and voltage 300 volts with the power circuit having 60 microfarads capacitance, 400 microhenries inductance, and 20 ohms resistance.

A ten percent rotating sector is used to limit the light coming from the arc. This amounts to reducing the original light intensity by ninety-five percent. The arc is then struck and allowed to burn for eighty seconds during which time the film is exposed.

The following element lines are read for low alloy steel:

<u>Element</u>	<u>Wave Length</u>
Fe	2840.4
Cr	2855.7
Si	2881.6
Mn	2933.1
Ni	3012.0
V	3110.7
Mo	3194.0
Al	3082.1

Calculations are made as in the point-to-plane analysis.

#### 4. Other Types of D. C. Arcs

Various methods of employing the D.C. arc have been investigated to test their suitabilities for this research program.

The first method investigated was a point-to-plane type. In order to keep the sample from becoming hot it was necessary to use a discharge of only one ampere.

The A.R.L. Multisource was set with 60 microfarads capacitance, 560 microhenries inductance and 150 ohms resistance. The sample was then excited in the same manner as in the point-to-plane spark technique.

This same excitation was used arcing to a rotating electrode. The sample, which was one-half inch in diameter, was mounted on the shaft of the motor for the A.R.L. solution excitation attachment. It was the positive and lower electrode and was rotated at the rate of twenty-five rpm. The exposure time was set at forty seconds. This latter method of excitation has the advantage over the point-to-plane in that it continually presents a fresh surface. This reduces the errors due to the inherent tendency of the D.C. arc to wander. These errors and the use of the rotating arc have received more complete attention by G. H. Dicke.<sup>6/</sup>

To investigate the possibilities of using fillings which are not volatilized to completion, an electrode, which we shall refer to as the "Inverted Cone Type", was employed. This was a graphite electrode .242 inches in diameter which had a cone shaped crater drilled in one end. This crater is filled level with fillings of the sample, and two drops of alcoholic sugar solution are added to reduce the blasting off of particles by the arc. The sample electrode was made positive with an analytical gap of two millimeters and the A.R.L. Multisource settings adjusted to produce a D.C. arc of four amperes. The sample was arced and the film exposed for three seconds.

## SECTION II

### PREPARATION OF STANDARDS

#### 1. Plan

In making standards for this program it was necessary to know the effect of one element on another independent of any other element in an iron matrix. In order to accomplish this with a minimum number of standards the scheme of fifty-two elements shown in Table I (Page 5) was devised. The three standards for each element with no extraneous element were to be used to establish a curve for intensity ratios within the range covered, free from the

TABLE I  
LIST OF SYNTHETIC STANDARDS SHOWING HOMOGENEITY  
AND COMPOSITION

Sample Number	Element	% Composition (Point-to-plane)				Extraneous Element	%Composition of Extraneous Element (Wet Value)
		Spectrographic		Wet			
12	Mn	.83	.78	.79	.80	None	
13	"	.39	.34	.36	.37	None	
14	"	.29	.32		.29	None	
1	"	.69	.72	.71	.69	Si	.92
3	"	.57	.57		.57	V	.32
15	"	.34	.36		.35	Ni	.57
16	"	.36	.37	.35	.35	Cr	.76
17	"	.43	.44		.40	Mo	.60
18	"	.70	.67		.74	Al	.56
19	"	.23	.23	.21	.22	Cu	.63
9	Si	.80	.83	.83	.83	None	
10	"	.19	.19	.19	.19	None	
11	"	1.18	1.19	1.27	1.23	None	
1	"	.94	.90	.92	.92	Mn	.69
7	"	.94	.94	.93	.94	Cr	.83
36	"	.12	.13	.12	.12	Ni	.55
37	"	.17	.19	.15	.17	Mo	.66
38	"	.25	.24	.22	.23	V	.26
39	"	.39	.39	.39	.42	Al	.44
40	"	.25	.23	.22	.23	Cu	.58
33	Ni	.52	.53	.51	.52	None	
34	"	.81	.82	.82	.82	None	
35	"	1.37	1.36	1.37	1.37	None	
15	"	.54	.58		.57	Mn	.35
36	"	.55	.55	.55	.55	Si	.12
41	"	1.10	1.12		1.14	Cr	.27
42	"	1.24	1.20		1.20	Mo	.69
43	"	1.07	1.07		1.07	V	.22
44	"	.56	.54		.56	Al	.51
45	"	.98	.98		1.00	Cu	.69
4	Cr	.84	.82	.80	.78	None	
5	"	.55	.55	.54	.41	None	
6	"	1.13	1.20	1.17	1.17	None	
7	"	.82	.83	.83	.83	Si	.94
8	"	.96	.96	.96	.96	V	.28
16	"	.77	.76	.76	.76	Mn	.35
41	"	.50	.51		.27	Ni	1.14
46	"	.65	.65		.39	Mo	.59
47	"	.68	.68	.67	.68	Al	.63
48	"	.71	.70		.43	Cu	.73



TABLE 1 (Cont'd)

Sample Number	Element	% Composition (Point-to-plane) Spectrographic				Extraneous Element	% Composition of Extraneous Element (Wet Value)
					Wet		
27	Mo	.66	.69	.68	.68	None	
28	"	.82	.82	.85	.82	None	
29	"	1.29	1.30	1.26	1.29	None	
17	"	.61	.59		.60	Mn	.40
37	"	.65	.67	.66	.66	Si	.17
42	"	.65	.65		.69	Ni	1.20
46	"	.57	.60		.59	Cr	.39
49	"	.71	.72		.75	V	.31
50	"	.84	.85		.80	Al	.58
51	"	.65	.66		.66	Cu	.68
20	V	.15	.15	.16	.15	None	
21	"	.19	.19	.20	.19	None	
22	"	.36	.36	.36	.36	None	
3	"	.32	.32		.32	Mn	.57
8	"	.28	.28	.28	.28	Cr	.96
38	"	.25	.27	.26	.26	Si	.23
43	"	.22	.21		.22	Ni	1.07
49	"	.30	.31		.31	Mo	.75
52	"	.30	.30		.30	Al	.66
53	"	.29	.30		.30	Cu	.57
30	Al	.44	.43		.43	None	
31	"	.52	.53	.53	.53	None	
32	"	1.07	1.07		1.07	None	
18	"	.55	.57		.56	Mn	.74
39	"	.45	.42	.44	.44	Si	.42
44	"	.46	.51		.51	Ni	.56
47	"	.62	.63	.63	.63	Cr	.68
50	"	.58	.57		.58	Mo	.80
52	"	.69	.66		.66	V	.30
54	"	.34	.36		.36	Cu	.39
24	Cu	.43	.43	.43	.43	None	
25	"	.71	.71	.68	.71	None	
26	"	1.02	1.08	1.02	1.02	None	
19	"	.65	.63	.61	.63	Mn	.22
40	"	.58	.57	.57	.58	Si	.23
45	"	.67	.70		.69	Ni	1.00
48	"	.75	.70		.73	Cr	.43
51	"	.69	.68		.68	Mo	.66
53	"	.57	.57		.57	V	.30
54	"	.40	.38		.39	Al	.36

Note: Those samples having but two values in the column "% Composition Spectrographic" are chill cast disks with analyses taken at the outside and center respectively, all others are crucible cooled heats with analyses taken at the upper right hand corner, the center and the lower left hand corner respectively.

influence of any extraneous elements. The other standards were to be used to determine intensity ratios within this range with the effect of an added extraneous element. These values could then be compared with the unaffected values for intensity ratios.

## 2. Apparatus

Power for melting the samples was supplied by a 15 K.V.A. induction unit manufactured by Lepel High Frequency Laboratories Inc., New York. A water cooled coil of ten turns made from 1/4 inch copper tubing and wound to fit closely around the crucible was electrically connected to the unit.

Both a graphite and a fire clay crucible were tested in connection with this unit. Using each of these crucibles 100 grams of a 4130 type steel in granular form was melted. Although the graphite crucible appeared to prevent the loss of any of the elements in the steel, there was considerable pick-up of carbon from the crucible. The fire clay was less successful in preventing loss of the elements due to oxidation, but there was no contamination of the sample tested. The fire clay crucible was chosen to be used in subsequent work since it resulted in no contamination and the percentage loss in the elements could to a certain extent be anticipated. This fire clay crucible, manufactured by the Denver Fire Clay Company of Denver, Colorado, is 4 inches in height, 2-3/8 inches in diameter at the top and 1-1/4 inches in outside diameter at the bottom.

## 3. Sintering and Melting with Metal Powder

Mechanical mixtures of pure iron powder and pure manganese powder were briquetted at a pressure of 75,000 lbs/sq in. and brought to white heat in the induction coil. While analysis of these briquettes showed no appreciable loss of manganese, they indicated that the samples lacked the desired homogeneity.

These same mixtures were melted, and in the process lost almost all of the manganese. Capping the charges with lime had no appreciable effect. It is believed that the particle size in these powders (300 mesh and finer) and consequently large surface area results in a considerable percentage of the sample existing as the oxide. The manganese would combine with the oxygen present as oxide and slag off. Since a large part of the oxides probably exist prior to melting, capping the melt or using an inert atmosphere would be futile.

#### 4. Melting with Armco Sheet Iron

In order to minimize as much as possible the surface presented for oxidation the elements were selected in sheet, bar or lump form. The forms of the elements were as follows: Iron as 5/16 inch wide strips of lengths from 1/4 inch to 1-3/4 inches cut from 1/16 inch Armco Magnetic Iron Sheet, manganese as lumps of ferromanganese, silicon as lumps of ferrosilicon, chromium as lumps of ferrochromium, vanadium as lumps of ferrovanadium, nickel from 1/4 inch pure nickel bar, molybdenum from 1/16 inch pure molybdenum bar, aluminum from 1/16 inch 2S aluminum bar and copper from 1/16 inch pure copper bar.

#### 5. Techniques Employed in Melting

The crucible is charged with 200 grams of iron. It is then placed in the coil, and with a power setting of 3 and a resonance setting of 12 the Lepel unit is turned on. After approximately 2 minutes and 20 seconds the iron charge comes to a rolling boil. At the end of three minutes the required amount of alloying element is added to the charge and the heating continued for an additional 15 seconds. The heat is then allowed to cool in the crucible or a second alloying element is added in the same manner as the first, whichever may be the case.

Some deviations from this procedure for the additions of the elements molybdenum, vanadium and aluminum are necessary. To obtain the desired degree of homogeneity in the standards containing molybdenum, it was found essential to continue the heating process for forty-five seconds after the addition to the molten iron or to add the molybdenum to the charge before heating. This latter alternative was found to be necessary in the case of vanadium since the ferrovanadium could not be forced through the slag layer into the molten iron. The vanadium would then become oxidized and subsequently give rise to gross segregation in the resulting melt.

The aluminum problem proved more difficult than either of these others. A 15 second heating period after the addition of the aluminum was found inadequate to produce a homogeneous sample. A 20 second period improved this condition but this was still inadequate. With periods of 30 seconds and longer the samples were found to contain large amounts of silicon. This was probably due to reduction of the silica in the clay crucible by the aluminum.

Using heats from 20 second heating periods, an attempt was made to homogenize them by soaking in a furnace at 2600°F for five hours. This attempt met with no success.

Acceptable standards containing aluminum were finally made by introducing

a pouring method of casting. In this method the aluminum is introduced into the charge 20 seconds before the end of the heating cycle. Immediately following the heating cycle the melt is poured from the clay crucible into a chill mold. This mold consists of a  $3/4$  inch thick steel chill plate and a two inch length of steel tubing of  $1-3/4$  inches inside diameter and  $2-1/2$  inches outside diameter. This section of tubing is placed upright on the chill plate and the melt poured into the upper end. It had been feared that considerable difficulty would be experienced in pouring these melts due to chilling by the sides of the clay crucible. This, however, was not the case, since there was little or no "skull" remaining in the crucible after the melt was poured.

## 6. Vacuum Melting

The success encountered in using the chill cast method led to the belief that perhaps N.B.S. wet chemical standard samples could be converted to a form suitable for spectrographic analysis with chemistry unchanged. By employing this technique and heating just to the melting point attempts were made on N.B.S. standards 30d, 32d and 139. Subsequent analyses of the resulting melts showed a loss in manganese content of approximately 15 percent, which indicated considerable oxidation taking place.

Since a suitable method for this conversion is considered a very useful tool for spectrochemical analysis, experiments were begun on vacuum methods of making the conversion. The first method used consists of partially filling a pyrex test tube with sample, evacuating with a vacuum pump and sealing off the test tube. (See Figure 4) This is then placed in a clay crucible which in turn is placed in the induction coil and brought to the melting point. (See Figure 5)

The second method consists of placing the charge directly in the crucible over which a bell jar is placed and partially evacuated. (See Figure 6) In this method it is not possible to evacuate the bell jar down to 1 millimeter of mercury as in the first method due to the low dielectric strength of the rarefied atmosphere. To avoid the corona effect occurring at pressures below approximately 80 millimeters of mercury the melts made in the bell jar were held at 120 millimeters of mercury.

Steels and stainless steels can be handled by either of these methods except for the element titanium, whereas brass can be handled only in the ampule method. Care must be taken with brasses to heat no longer than is necessary to melt them and to avoid cold spots on the ampule. These cold spots cause condensation of zinc with consequent enhancement of distillation from the brass. This can be partially eliminated by introducing argon at a pressure of about 100 millimeters of mercury.

Table II gives results of melting various N.B.S. wet chemical standards by these methods.

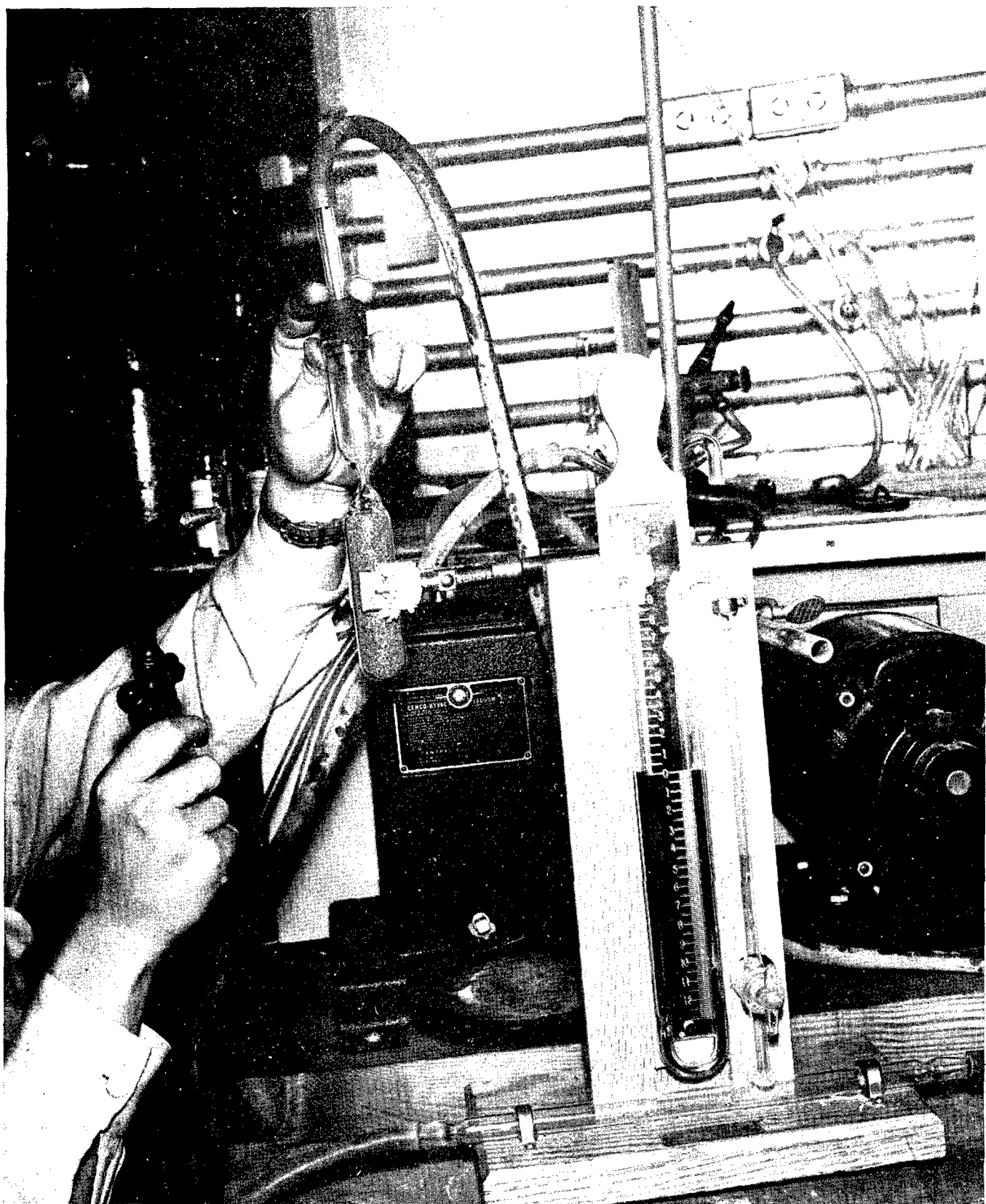


Figure 4 Sealing Sample in Evacuated Pyrex Test Tube



Figure 5 Evacuated Test Tube Ready for Melting

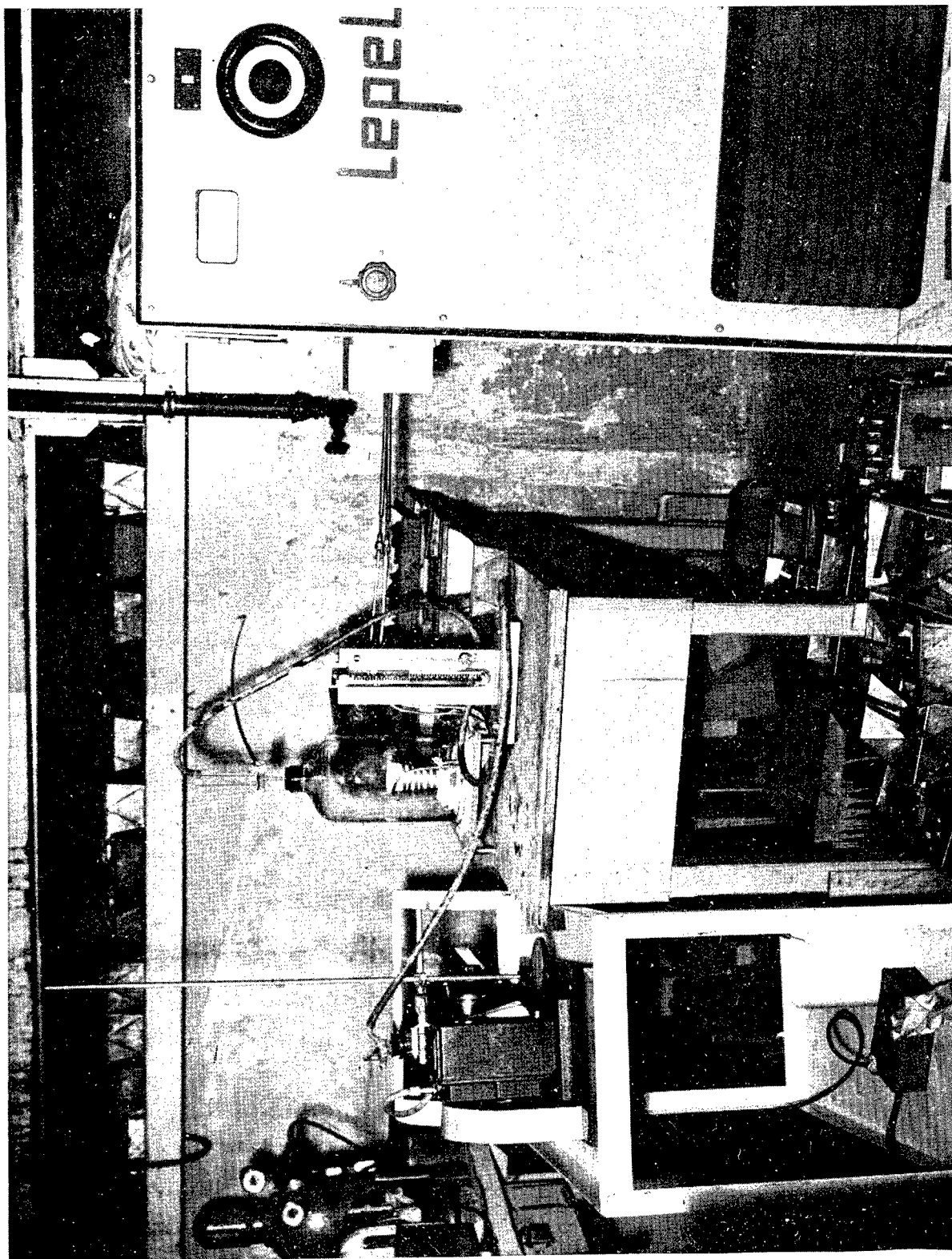


Figure 6 Melting Sample Under Controlled Pressure

TABLE II

COMPARISON OF MELTED N.B.S. STANDARD SAMPLES  
WITH ORIGINAL N.B.S. VALUES

Sample Number	Element	% Composition		Wet	Method of Melting
		Spectro.	Bureau of Standards		
139	Mn	.86	.867	.89	Bell Jar
	Si	.28	.292		
	Ni	.55	.563		
	Cr	.55	.549		
	Mo	.18	.178		
121b	Mn	1.50	1.52	1.47	Ampule
	Si	.55	.596		
	Ni	11.25	11.14		
	Cr	17.60	17.68		
	Ti	.13	.416		
	Cu	.10	.12		
101C	Mn	.65	.64	.64	Bell Jar
	Si	.56	.59		
	Ni	9.25	9.27		
	Cr	18.10	18.21		
	Cu	.13	.12		
62B	Cu	57.70	57.39	57.22	Ampule
	Sn	.96	.96		
	Zn	37.60	37.97		
	Fe	.87	.82		
	Mn	1.27	1.29		
	Si	.05	.048		
	Pb	.22	.28		
	Ni	.30	.27		
	Al	1.02	.97		
52C	Cu	89.35	89.25	89.29	Ampule
	Sn	7.80	7.85		
	Zn	2.10	2.12		
	Ni	.75	.76		



### SECTION III

#### QUALITY CONTROL OF STANDARDS

Heats which had been crucible cooled were cut lengthwise through the center. Those that were chill cast were cut edgewise through the center. One face from these cuts was prepared and analyzed by the spectrographic point-to-plane technique. The crucible cooled samples were analyzed at opposite corners and the center of the sample, and the chill cast samples were analyzed at one spot on the edge and at the center. Preliminary tests had indicated that where segregation did occur in this type it tended to be from outside to center. This was perhaps due in part to the relatively thin disk (1/4 in. to 3/8 in.)

Preliminary spectrographic analyses were used to establish the following conditions: (1) freedom from contamination, (2) alloying elements within desired concentration range and (3) homogeneity of sample. Standards which satisfied these conditions had millings taken from an entire cut surface for wet chemical analysis. (See Table I Page 7 )

The point-to-plane spark type of analysis was used to check for segregation due to the negligible effect of one element on the line intensity of another. A large number of steel samples have been analyzed in this laboratory without encountering any inter-element effects with the use of this technique. This same technique has been used to determine segregation in aluminum alloys.7/

This assumption is also borne out by the good agreement (See Table I) between wet and spectrographic values arrived at in this program. The only discrepancies of any magnitude were in the case of certain values of chromium. These values have undergone considerable investigation (See Table III) to determine the cause of the discrepancies. These discrepancies cannot be ascribed to any inter-element effect because they occur not only when copper, nickel and molybdenum are present but when chromium alone is present. In addition to this, the same analytical curve is used on production steels which contain all of these elements, and no discrepancies are encountered.

It is noteworthy that the same sort of discrepancies appear in the platform-arc type of analysis described in Section V.

TABLE III  
REPRODUCIBILITY OF PERCENTAGE CHROMIUM VALUES  
SPECTROGRAPHIC AND WET CHEMICAL

Sample Number	Run	% Cr Spectrographic			% Cr Wet		Extraneous Element Percentage
					Reference Method	Perchloric Acid Oxidation	
4	1st	.84	.82	.80	.78	.78	None
4	2nd	.83	.83	.80	.77		"
4	3rd	.85	.80	.83	.78		"
5	1st	.55	.55	.54	.41	.42	"
5	2nd	.55	.54	.55	.42		"
5	3rd	.55	.55	.54	.41		"
6	1st	1.13	1.20	1.17	1.17	1.18	"
6	2nd	1.17	1.19	1.21	1.19		"
6	3rd	1.14	1.18	1.20	1.16		"
7	1st	.82	.83	.83	.83	.83	Si .94
7	2nd	.83	.82	.83	.82		"
7	3rd	.83	.83	.83	.83		"
8	1st	.96	.96	.96	.96	.96	V .28
8	2nd	.95	.96	.96	.96		"
8	3rd	.96	.96	.96	.95		"
16	1st	.77	.76	.76	.76	.77	Mn .35
16	2nd	.76	.76	.76	.77		"
16	3rd	.76	.76	.76	.76		"
41	1st	.50	.51		.27	.29	Ni 1.14
41	2nd	.50	.50		.28		"
41	3rd	.51	.50		.27		"
46	1st	.65	.65		.39	.38	Mo .59
46	2nd	.65	.65		.37		"
46	3rd	.65	.65		.39		"
47	1st	.68	.68	.67	.68	.67	Al .63
47	2nd	.68	.68	.68	.68		"
47	3rd	.67	.68	.67	.67		"
48	1st	.71	.70		.43	.45	Cu .73
48	2nd	.70	.70		.41		"
48	3rd	.71	.71		.43		"

## SECTION IV

### INVESTIGATION OF THE D.C. ARC

Before attempting to accomplish the purpose of this research program it was felt that various types of D.C. arcs should be tried to find the most reproducible. A preliminary investigation was begun by making several runs on the same sample (a vanadium steel) by the point-to-plane D.C. arc, point to a rotating disk and the platform arc. The latter was tried with a stream of air being drawn past the arc to reduce self-absorption of the spectral lines.

The results of these runs are shown in Tables IV, V, VI and VII. The change in the log of the intensity is tabulated rather than the intensity ratio merely for convenience. It can be shown that lines having the same change in the log of the intensity in the same columns are homologous. From these results it was decided that except for the point-to-plane arc these methods resulted in approximately equal reproducibilities.

The Inverted Cone Type electrode was used on the standards of this program which contained silicon. The results of these runs are tabulated in Table VIII.

The runs where blanks are shown yielded spectrograms too light to read.

The discrepancies shown by these runs are too great to allow any evaluation of inter-element effects unless a very large number of runs were to be made to average out differences.

The erratic behavior of this type excitation can be explained by the fact that the arc can strike either the edge of the graphite electrode or the solid sample indiscriminately. It was noticed on those runs where the spectrograms were extremely light that the arc travelled about the periphery of the cup for almost the entire duration of the arcing period.

It was felt that the rotating disk type of excitation was impractical for this investigation. There was not only the difficulty of machining a disk from the sample, but there would be very few lines of high excitation potential to choose from due to the very low voltage employed across the gap.

The platform arc type of excitation was then used to set up analytical curves for all of the elements under consideration by means of the standards of this program. These curves are shown in Figures 4, 5, and 6.

TABLE IV  
LINE INTENSITY CHANGES  
FOR POINT TO ROTATING CYLINDER ARC

<u>Wave Length</u>	<u>Element</u>	<u><math>\Delta \log I</math></u>		
		<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>
2880.8	Fe	-.07	.00	.01
2881.6	Si	-.03	.01	.06
2901.4	Fe	-.3	.01	.02
2901.9	Fe	-.13	.02	.02
2899.4	Fe	-.10	.04	.07
2918.0	Fe	-.16	.04	.08
2920.7	Fe	-.15	.00	.02
2923.3	Fe	-.10	.01	.04
2923.9	Fe	-.13	.03	.11
3014.9	Cr	-.19	.03	.16
3414.8	Ni	-.04	.07	.04

TABLE V

## LINE INTENSITY CHANGES FOR PLATFORM ARC

Wave Length	Excitation Potential	Element	$\Delta \text{Log I}$		
			Run 2	Run 3	Run 4
2855.7	15.42	Cr	.02	.10	.15
2858.9	4.45	Fe	.01	.10	.13
2865.1	12.60	Cr	.01	.08	.13
2867.6	5.93	Fe	-.01	.12	.14
2872.3	5.27	Fe	.01	.11	.17
2874.2	4.32	Fe	-.03	.06	.13
2877.3	5.79	Fe	.06	.11	.16
2880.8	13.15	Fe	-.05	.07	.13
2881.6	5.08	Si	-.01	.09	.10
2894.5	6.56	Fe	.02	.10	.13
2895.2	16.04	Fe	.00	.09	.14
2899.4	6.55	Fe	-.03	.08	.16
2901.4	5.83	Fe	.02	.10	.14
2901.9	6.67	Fe	.01	.11	.16
3414.8	3.66	Ni	-.03	.05	.11
3415.5	5.85	Fe	-.01	.07	.11
2933.0	12.85	Mn	.07	.12	.14
3102.3	11.10	V	-.06	.08	.11
3110.7	11.07	V	-.05	.10	.18
3236.8	5.97	Mn	-.02	.07	.17
3274.0	3.80	Cu	.00	.05	.13

TABLE VI  
LINE INTENSITY CHANGES FOR PLATFORM ARC  
(MOVING AIR STREAM)

<u>Wave Length</u>	<u>Element</u>	<u><math>\Delta \text{Log I}</math></u>		
		<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>
2855.7	Fe	.04	.10	.10
2858.9	Fe	.09	.12	.11
2865.1	Fe	.12	.11	.10
2869.3	Fe	.16	.24	.08
2874.2	Fe	.17	.22	.10
2877.3	Fe	.08	.12	.10
2880.8	Fe	.09	.12	.07
2881.6	Si	.14	.16	.16
2894.5	Fe	.13	.13	.12
2895.2	Fe	.10	.13	.14
2899.4	Fe	.07	.11	.11
2901.4	Fe	.11	.11	.13
2901.9	Fe	.09	.11	.15
3414.8	Ni	.10	.21	.11
3415.5	Fe	.07	.07	.10
2933.0	Mn	.11	.11	.06
3102.3	V	.04	.05	.04
3110.7	V	.08	.13	.13

TABLE VII

## LINE INTENSITY CHANGES FOR POINT-TO-PLANE ARC

Wave Length	Element	Excitation Potential	$\Delta \log I$				
			Run 2	Run 3	Run 4	Run 5	Run 6
2858.9	Fe	4.45	-.03	.42	.47	.29	.26
2874.2	Fe	4.32	-.09	.29	.33	.29	.08
2877.3	Fe	5.79	-.06	.41	.44	.29	.20
2880.8	Fe	13.15	-.06	.32	.31	.17	.13
2894.5	Fe	6.56	-.05	.44	.46	.27	.24
2895.2	Fe	16.04	.03	.43	.46	.25	.21
2899.4	Fe	6.55	-.03	.43	.47	.24	.27
2901.4	Fe	5.83	-.04	.44	.49	.31	.28
2901.9	Fe	6.67	.02	.48	.52	.30	.29
3011.5	Fe	6.88	-.08	.44	.43	.22	.24
3151.4	Fe	6.66	-.04	.43	.43	.22	.29
3153.2	Fe	6.38	-.02	.41	.43	.24	.27
3280.3	Fe	7.08	-.04	.43	.47	.23	.29
3291.0	Fe	5.98	.05	.36	.40	.21	.24
3292.0	Fe	7.02	-.05	.44	.49	.27	.29
3292.6	Fe	5.99	-.05	.42	.47	.30	.32
3314.7	Fe	7.05	-.04	.42	.41	.24	.26
3370.8	Fe	6.37	-.02	.49	.52	.28	.29
2881.6	Si	5.08	-.12	.16	.33	.11	.24
2933.1	Mn	12.85	.05	.42	-.41	-.53	-.20

TABLE VIII

SPECTROGRAPHIC RESULTS OBTAINED  
USING THE INVERTED CONE TYPE ELECTRODE

<u>Sample Number</u>	<u>% Si</u>	<u>Run Number</u>	<u><math>\frac{I_{Si}}{I_{Fe}}</math></u>
9	.83	1	1.86
		2	2.66
10	.19	1	1.48
		2	1.14
11	1.23	1	1.13
		2	2.5
1	.92	1	2.03
		2	--
7	.94	1	2.8
		2	2.04
36	.12	1	.815
		2	.76
37	.17	1	1.27
		2	--
38	.23	1	1.40
		2	.88
39	.42	1	.63
		2	1.27
40	.23	1	1.27
		2	--



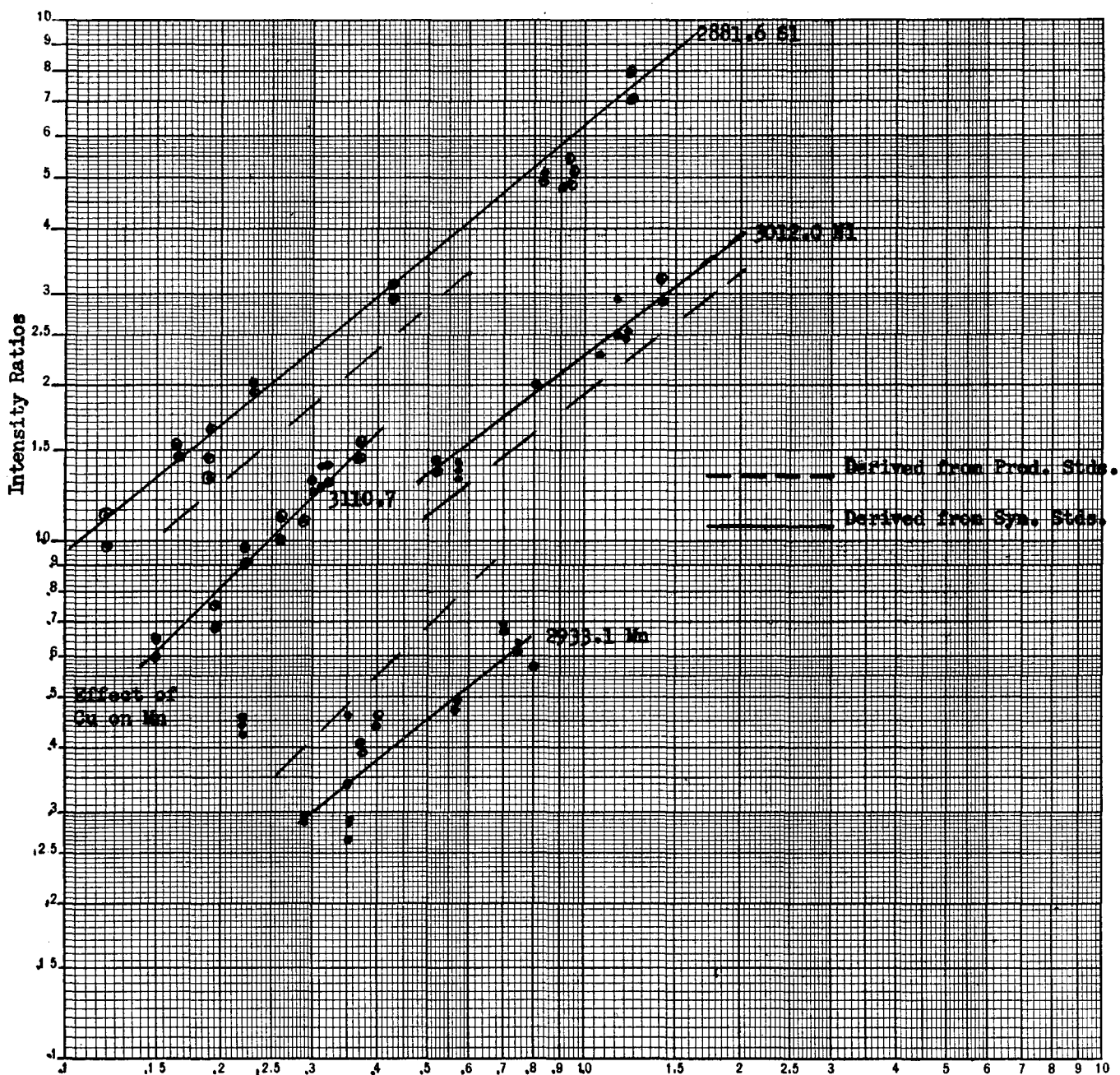


Fig. 7 Element Percentages

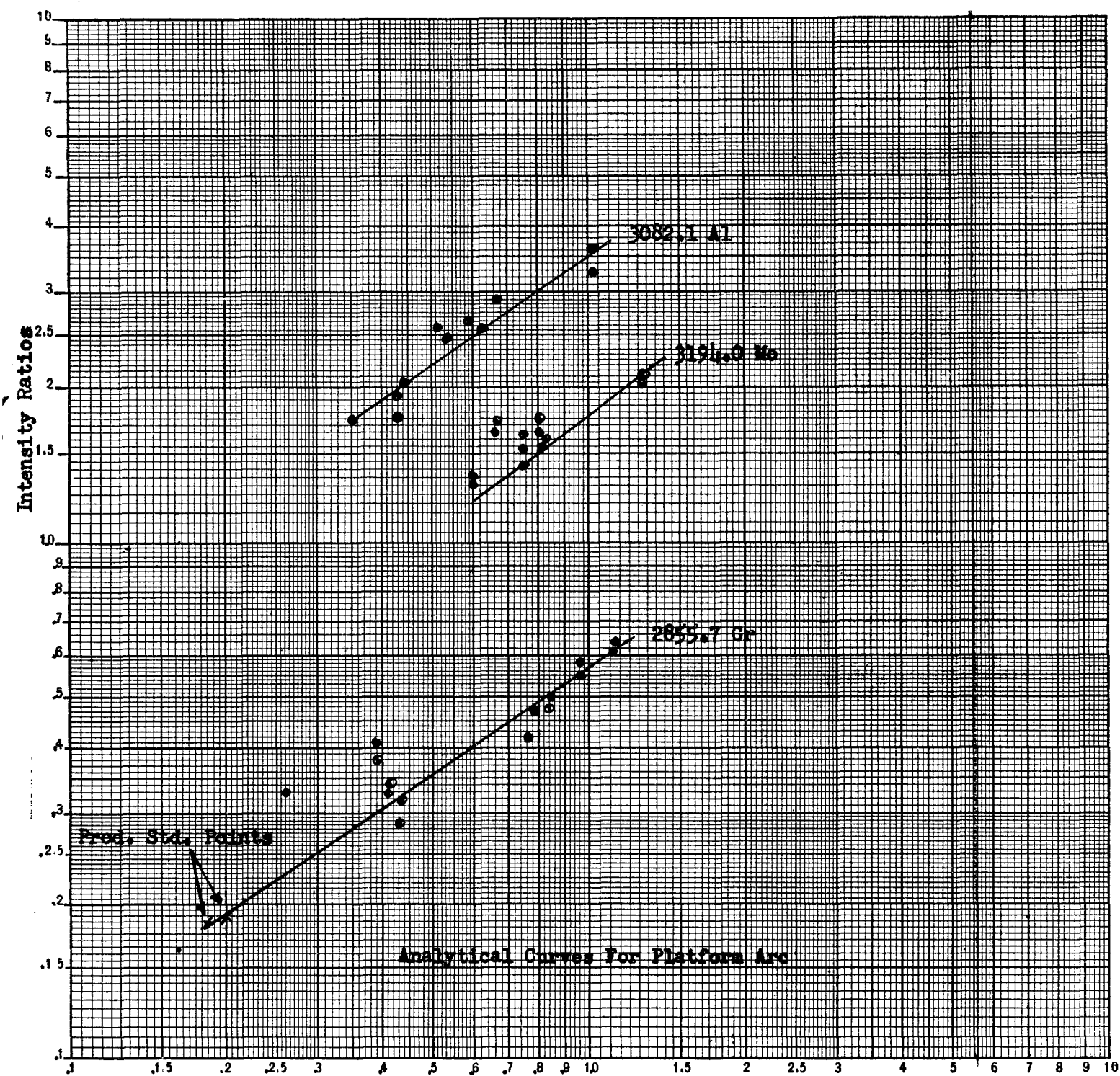


Fig. 8 Element Percentages

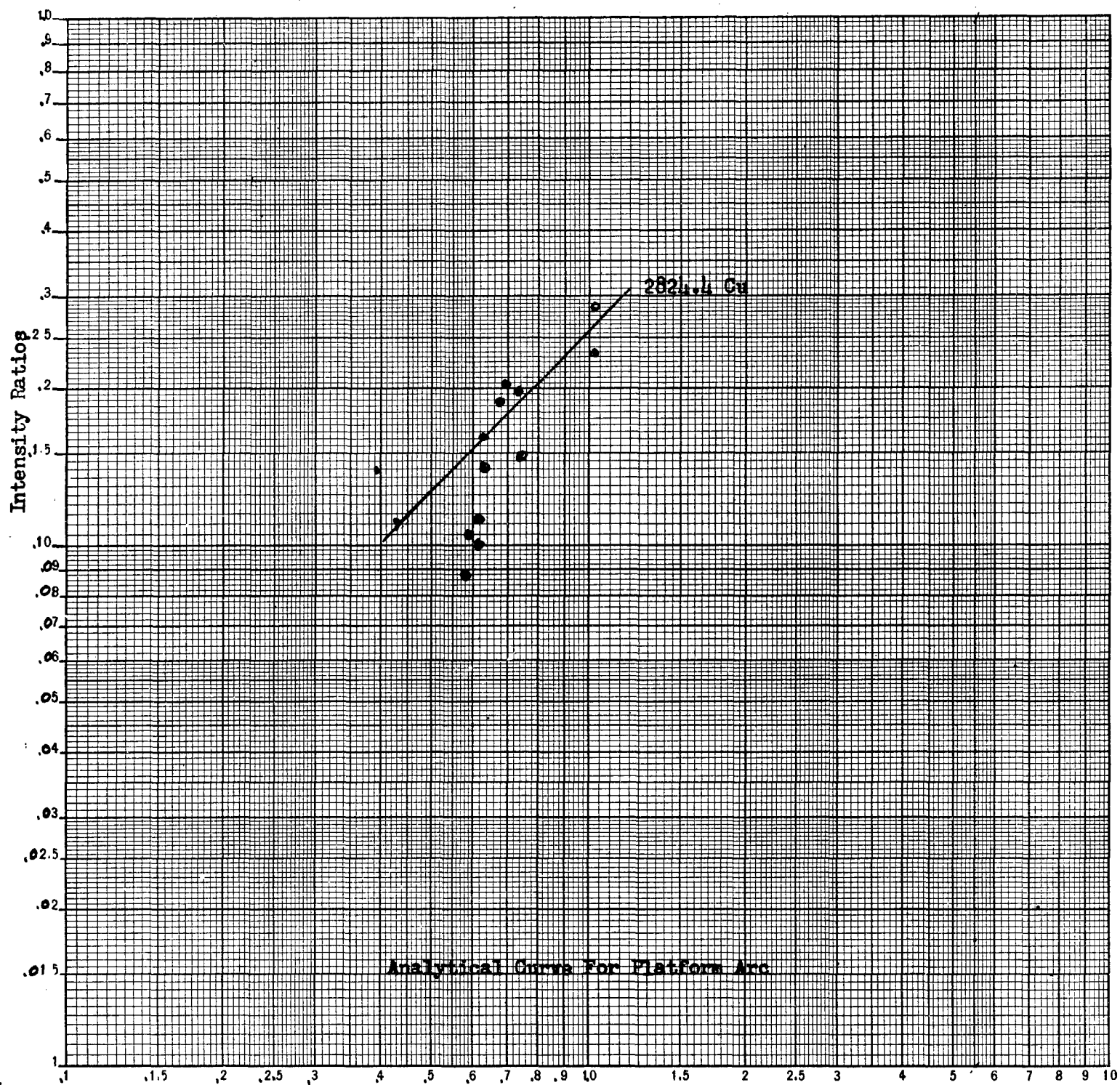


Fig. 9 Element Percentages

## SECTION V

### EFFECTS OF EXTRANEOUS ELEMENTS

The most marked effects encountered in this research program are the discrepancies in the analytical curves for low chromium values. This effect is all the more remarkable in that it was found in the point-to-plane spark type analysis as well as in the platform arc.

In order to establish this discrepancy in chromium values more certainly, several of the standards used for ordinary production samples were run. The values for the chromium percentages and the intensity ratios obtained are shown in Table IX. These values fit the curve for chromium (Figure 5) very well, so two of the points marked "x" were used to extend the chromium curve to lower values.

These discrepancies obviously cannot be accounted for on the basis of effects caused by elements considered here because the production standards used contain molybdenum and nickel in various combinations and yet reflect no influence as compared to standards which do not contain these elements.

There is one thing common to these standards having low chromium values - they all lack an effective de-oxidizing element. A graph comparing the de-oxidizing powers of seven alloying elements as a function of their percent composition at 2900°F is given by the "Committee on the Physical Chemistry of Steelmaking A. I. M. E." 8/

In general their effectiveness is in the following order: aluminum, titanium, vanadium, silicon, carbon, manganese and chromium.

It is interesting to note that at approximately 1.0%, the chromium curve approaches that of the manganese. This may explain why the two standards containing only chromium at higher values do not exhibit this peculiarity.

In employing the production standards for setting up analytical curves for the platform arc, it was found that the curve was shifted appreciably from that obtained by using the synthetic standards of this program. The curve for the production standards is shown by a dashed line in Figure 4. The nickel curve for production standards (also dashed line Figure 4) also shows a shift from the other standards.

Due to a lack of standards in the range involved the shifts in the curves for the other elements cannot be determined with any accuracy, but the silicon

TABLE IX

TABLE OF VALUES OBTAINED USING PRODUCTION  
STANDARDS WITH THE PLATFORM ARC

<u>Element Investigated</u>	<u>Percentage</u>	<u>Intensity Ratio</u>	<u>Standard Number</u>
Mn	.34	.46	801
"	.38	.51	810
"	.46	.61	802
"	.52	.71	818
Cr	.20	.19	809
"	.18	.185	805
"	.49	.34	4
"	.51	.34	5
Ni	.58	1.30	5
"	.49	1.18	4
"	1.21	2.20	808

curve appears to show a shift as indicated by the dashed lines Figure 4, and the molybdenum appears to be unaffected by the type of standard used.

It is obvious that these shifts cannot be attributed to the effect of any element considered in this investigation. One of the production standards used (standard No. 801) contained manganese as the only alloying element, yet it plots on the curve given by the dashed line. Standard No. 14, which also contains manganese only, plots considerably to the right of this curve.

One would expect no effect from metallurgical history to occur in the platform arc since the sample is melted almost immediately thereby erasing any of the previous physical history.

The most likely explanation seems to be that these phenomena are caused by carbon or oxygen, which have not been considered in this investigation.

The only element effect which appears to have been caused by an element considered in this investigation is the effect of copper on the manganese. The three points for standard No. 19, which contains copper, are shown in Figure 4 considerably to the left of even the manganese curve for the production standards. The 2939.6 manganese line was read and its ratio to the iron line plotted against percent manganese but it gave the same type of curve as the 2933.1 manganese with the point for standard No. 19 in the same relative position. The likelihood of an unlisted interference occurring on both manganese lines is very small. In production there have never been values as high on copper, so there is no way of further checking this phenomenon. It is not unlikely that this too could be explained by the influence of carbon or oxygen.

## SECTION VI

### LINE PAIR INVESTIGATION

Virtually all quantitative work in the past by this laboratory has been done by the point-to-plane spark type of analysis. As a consequence the line pairs used with this method have not only been carefully studied, but they have undergone a rigorous empirical elimination process due to the large number of steels analyzed.

It has been found necessary not only to select lines which are free from self-absorption and interferences but also to pair them so that the excitation

potentials are close together. (See Table X) Hasler and Kemp, <sup>9</sup>/ Hurwitz and Convey<sup>10</sup>/ and others have also suggested the desirability of selecting line pairs on this basis.

An investigation of line pairs for the platform arc, however, indicates no such dependence upon excitation potential. Tables X and XI show no improvement in reproducibility where the line pairs were well chosen by the above criterion as compared to those which were poorly selected.

## SECTION VII

### DISCUSSION AND CONCLUSION

There are a number of effects which might be and have in the past been termed "influence of one element on the other." Among these is what might be called a dilution effect, due to the decrease in percentage of the principal constituent by virtue of adding an extraneous element. This effect has been accounted for in various ways by different authors. 11,12,13,14/

Another effect is that due to fractional volatilization of the elements in the sample. Extraneous elements can affect this by raising or lowering the boiling point of the sample.

The first effect mentioned is not a factor due to the fact that all the extraneous elements were considered in concentrations of less than one percent which is less than the error inherent in usual spectrographic techniques. The second effect is practically eliminated by volatilizing the sample to completion. This effectively integrates the total energy emanating from each of the elements concerned.

In eliminating these two effects we enhance the possibility of ascertaining other causes which might give the same effect. Besides, it was found in this program that this type of arc is superior to others with regard to reproducibility. (See Section IV)

Another factor which reduces influence of one element on the other is the narrow analytical gap employed. It was found in earlier work in this laboratory that a wide gap tends to enhance the effect of one element on the line intensity of another.

TABLE X  
LINE PAIR RELATIONSHIPS FOR POINT-TO-PLANE  
SPARK METHOD OF ANALYSIS

<u>Element</u>	<u>Element Line</u>	<u>Excitation Potential</u>	<u>Transition</u>	<u>Iron Internal Standard Line</u>	<u>Excitation Potential</u>	<u>Transition</u>
Mn	3460.3	12.77	$^5D_3 - ^5P_2^{\circ}$	3277.3	12.59	$^4D_{3-1/2} - ^6D_{4-1/2}^{\circ}$
V	3110.7	11.07	$^5F_3 - ^5G_4^{\circ}$	"	"	"
Mo	2816.2	11.93	$^6D_{4-1/2} - ^6F_{5-1/2}^{\circ}$	"	"	"
Cr	3118.7	13.10	$^4D_{1/2} - ^4F_{1-1/2}^{\circ}$	"	"	"
Cr	3408.8	12.83	$^4D_{3-1/2} - ^4P_{2-1/2}^{\circ}$	"	"	"
Ni	3414.8	3.64	$^3D_3 - ^3F_4^{\circ}$	3199.5	3.96	$^5D_1 - ^3F_2^{\circ}$
Al	3082.1	4.00	$^2P_{1/2}^{\circ} - ^2D_{3-1/2}$	"	"	"
Cu	3274.0	3.77	$^2S_{1/2} - ^2P_{1/2}^{\circ}$	"	"	"
Si	2881.6	5.06	$^1D_2 - ^1P_1^{\circ}$	"	"	"



TABLE XI

REPRODUCIBILITY COMPARISONS FOR VARIOUS  
LINE PAIR RELATIONSHIPS IN PLATFORM ARC METHOD

Sample Number	Run	Element	Element Line	Iron Line	Line Ratio	State of the Atom	
						(I) Normal	(II) Once Ionized
18	1st	Mn	2933.1	2840.4	.77	Mn II	Fe I
18	2nd	"	"	"	.80	"	"
18	3rd	"	"	"	.82	"	"
18	1st	Mn	2933.1	3196.1	.91	Mn II	Fe II
18	2nd	"	"	"	.98	"	"
18	3rd	"	"	"	1.00	"	"
18	1st	Mn	2801.1	2840.4	1.18	Mn I	Fe I
18	2nd	"	"	"	1.27	"	"
18	3rd	"	"	"	1.33	"	"
47	1st	Cr	2855.7	2840.4	.60	Cr II	Fe I
47	2nd	"	"	"	.59	"	"
47	3rd	"	"	"	.54	"	"
47	1st	Cr	2855.7	3196.1	.75	Cr II	Fe II
47	2nd	"	"	"	.73	"	"
47	3rd	"	"	"	.66	"	"
52	1st	V	3110.7	2840.4	1.18	V II	Fe I
52	2nd	"	"	"	1.23	"	"
52	3rd	"	"	"	1.22	"	"
52	1st	V	3110.7	3196.1	1.49	V II	Fe II
52	2nd	"	"	"	1.48	"	"
52	3rd	"	"	"	1.49	"	"

TABLE XII

LINE PAIR RELATIONSHIPS  
FOR PLATFORM ARC METHOD OF ANALYSIS

Element Line	Excitation Potential	Transition
2840.4 Fe I	4.40	$^5D_3 - ^5G_3^0$
3196.1 Fe II	13.32	$^4P_{2-1/2} - ^4F_{3-1/2}^0$
2933.1 Mn II	12.78	$^5S_2 - ^5P_1^0$
2801.1 Mn I	4.43	$^6S_{2-1/2} - ^6P_{1-1/2}^0$
2855.7 Cr II	12.54	$^6D_{1-1/2} - ^6F_{2-1/2}^0$
3110.7 V II	11.07	$^5F_3 - ^5G_4^0$
2939.3 Mn II	12.77	$^5S_2 - ^5P_2^0$

In addition to these considerations, it is generally believed that elements occurring in small quantities (less than one percent) have no effect on the line intensity of other elements, <sup>15/</sup> so it would have been expected in this research program that no inter-element effects would be encountered. We used these quantities, however, since they represent the magnitude of percentages ordinarily found in low alloy steel. In the elements studied, i.e. chromium, manganese, silicon, nickel, molybdenum, vanadium, aluminum and copper, the results were almost as would be expected. The only effect of any magnitude that might possibly have been one on the other would be that of copper on the manganese line.

On the other hand, if these effects had not been minimized to the extent that they were, the much more unusual effects encountered would probably have escaped us. These effects are: namely, the discrepancies in the chromium line for low values of chromium, and the shift in working curves for manganese, silicon, and nickel when using the synthetic standards developed in this program rather than ordinary steels.

These results are all the more remarkable when it is considered what a small percentage of extraneous element would be concerned if they are due to the elements carbon, oxygen, phosphorus or sulfur. Any one of these would be concerned in percentage values less than 0.1, and as pointed out before, <sup>15/</sup> percentages of extraneous elements less than one percent have been considered to have little or no effect on other element lines.

It seems that the answer to these effects must be found before attempting a broader approach to the problem. It is necessary in determining other inter-element effects, either to hold these factors constant or to correct for them. With our present knowledge of these phenomena neither alternative is possible.

It is obvious from the foregoing discussion that a series such as that proposed by Brode and Timma <sup>3/</sup> could not be established on the basis of the work done here.

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